COAL/OIL COPROCESSING USING SYNGAS: EFFECTS OF D_2O DURING HYDRODESULFURIZATION

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INTRODUCTION

It has been shown that coal liquefaction[1] and coprocessing[2,3] of coal with petroleum solvents could be carried out using syngas (H_2+CO) and steam instead of hydrogen. High coal conversion could be obtained with considerable saving in hydrogen consumption. Earlier studies have also shown that model compounds could be hydrogenated and desulfurized in the presence of petroleum solvents and catalyst using syngas with steam. It was considered that the CO in the syngas reacts with steam to form hydrogen via water-gas shift reaction, and that the hydrogen formed could also participate in the hydrogenation of coal, but the fate of hydrogen formed from the water-gas shift reaction was not known. It is known that deuterium is incorporated into reaction products during coal liquefaction under D_2 gas[4], and that hydrogen/deuterium transfer occurs among solvent, reaction products and gas when deuterium-labled solvents are used in coal liquefaction experiments[5].

This study deals with hydrodesulfurization of a sulfur-containing model compound using syngas and steam. In order to understand the roles of molecular hydrogen and water in the syngas system during the hydrodesulfurization, experiments were carried out to treat dibenzothiophene in the presence of solvent and catalyst under pressure using H_2-CO-D_2O, D_2-CO-H_2O and N_2-D_2O systems. Deuterium gas and D_2O were used in an effort to study the incorporation of hydrogen from the gas and water by tracing the migration of deuterium through the system.

EXPERIMENTAL

The hydrodesulfurization of dibenzothiophene was conducted in a shaking 25-ml microreactor in the presence of decalin solvent and a commercial NiMo/Al_2O_3 catalyst(Nippon Mining Co.) using syngas and water at an initial pressure of about 70 kg/cm^2 in most cases. The reactor was quickly heated up in a fluidizing sand bath and maintained at 400℃ for 45 minutes, and then rapidly quenched in a cold water bath. Various H_2:CO:H_2O mole ratios with H_2/CO mole ratios varying from 1 to 3 and H_2O/CO mole ratios varying from 0.3 to 1.0 were used. For the experiments, a mixture of 30 parts of dibenzothiophene and 70 parts of solvent was placed in the microreactor, 10 weight %(based on the mixture) of ground presulfided catalyst was charged, and calculated amount of water was added before the reactor was pressured with syngas. After the reaction, the liquid products were analyzed by a Shimadzu GC-14A gas chromatograph using OV-1 fused silica capillary column(60m× 0.25mmϕ), and gasous products were analyzed by a Shimadzu GC-14A gas chromatograph.

In experiments using D_2 gas and D_2O, an initial pressure of about 40 kg/cm^2 was used because of low pressure available for the D_2 bomb. The liquid products were analyzed by a Shimadzu QP-1000 gas chromatograph-mass spectrometer. Spectral analysis was performed using the known split patterns of various undeuterated compounds. For these runs, samples of the gaseous products were obtained by passing through a dry ice and acetone trap to remove moisture prior to analysis using gas chromatograph and a ULVAC MSQ-150A quadrapole mass analyzer. For hydrogen analysis, relative intensities of peaks of molecular ions were used to estimate the relative portions of H_2, HD, and D_2.

RESULTS AND DISCUSSION

Hydrodesulfurization of Dibenzothiophene in Various Solvents. During coal liquefaction, large coal molecules fragment thermally and are hydrogenated via hydrogen transfer from a donor solvent. Coprocessing of coal with petroleum solvents using either hydrogen or syngas with steam was also aided by the presence of tetralin[3]. Dibenzothiophene was initially hydrodesulfurized in the presence of various solvents including decalin, tetralin, and a mixture of decalin and an aromatic compound. The results of hydrodesulfurization carried out under hydrogen and syngas pressures are shown in Table 1. Dibenzothiophene was easily hydrogenated and desulfurized by hydrogen to form mainly biphenyl, cyclohexylbenzene, bicyclohexyl, and decomposed products. Tetralin donated some hydrogen to form naphthalene, but was also hydrogenated to form decalin. Decalin converted to small amounts of tetralin and naphthalene. An aromatic compound was added with an intention of finding out the effects of aromatic compounds on hydrogen transfer between decalin and dibenzothiophene. The hydrogenated products from 1-methylnaphthalene was not included in the table. When an aromatic compound was added to decalin as the solvent, the effect on the product distribution was not conclusive, but high dibenzothiophene conversions were obtained with all solvents. It appears that catalytic hydrogenation by hydrogen gas plays the dominant role with respect to the hydrodesulfurization.

When dibenzothiophene was treated with syngas and steam (H_2:CO:H_2O=1:1:0.3), the hydrogenation and desulfurization activeties were lower. The yields of hydrogenated products, cyclohexylbenzene and bicyclohexyl, were lower. These results indicate that the performance of syngas in hydrodesulfurization did not come up to the satisfactory level that was observed in coal liquefaction. In coal liquefaction, the performances with syngas and H_2 compare rather closely except that asphalten levels of the syngas products were somewhat higher[1].

Table 2 shows the results of hydrodesulfurizing dibenzothiophene using decalin solvent and syngas with steam at various H_2:CO:H_2O ratios. The dibenzothiophene conversion increased with H_2/CO mole ratio, while H_2O/CO mole ratio was maintained at 0.6. The data indicate that the H_2O level at the H_2O/CO mole ratio of about 0.6 is appropriate or about optimum to give better results yielding more hydrogenated products. The extent of water-gas shift reaction was rather extensive as can been seen from high CO conversions obtained in all runs. The CO conversions were calculated on the basis of the amounts of CO_2 formed. As was observed in coal liquefaction and coprocessing using syngas, H_2 formation via water-gas shift reaction resulted in reduction of hydrogen consumption and increase of H_2/CO mole ratio after the reaction.

Hydrodesulfurization Using Syngas Containing D_2O and D_2. Experiments with syngas containing D_2O and D_2 were carried out to observe how the hydrogen transfer reactions occured from H_2O and gas-phase hydrogen. Dibenzothiophene was hydrodesulfurized in the presence of decalin solvent using H_2-CO-D_2O(1:1:1) and D_2-CO-H_2O(1:1:1) gas systems as shown in Table 3. Another experiment using N_2-D_2O(2:1) system was also carried out. Initial pressures of syngas and N_2 used were lower(about 40 kg/cm^2) in this series of experiments because only a limited pressure of D_2 gas was available. Similar to the results shown in Table 2, both the hydrodesulfurization and water-gas shift reaction progressed moderately. In the experiment using N_2-D_2O system, some dibenzothiophene decomposed to form biphenyl, and the formation of naphthalene from decalin increased.

The reaction products and remaining solvents were analyzed using GC-MS, and deuterium distributions in the products and solvents are shown in Figure 1. In the H_2-CO-D_2O system, the cyclohexylbenzene product was deuterated extensively to form d_2, d_3, d_4, d_5, and d_6 species, but no d_0 or d_1 species was present. Deuterium was also distributed widely to the biphenyl product, and all species from d_0 to d_6 were present. Large parts of cis-decalin was isomerized to trans-form, but both forms similarly contained about 30% of d_1-decalin. Only trans-decalin was shown in Figure 1. The H/D exchange of D_2O with the decalin solvent was not as extensive as that with the products. In the D_2-CO-H_2O system, it was noted that deuterium was incorporated only moderately into cyclohexylbenzene and biphenyl, both forming d_1, d_2, and d_3 species. Only about 20% of d_1 species was present in either trans- or cis-decalin. It is of interest to observe that, under N_2 pressure, H/D exchange occured extensively between D_2O and dibenzothiophene. Even though the amounts of cyclohexyl and biphenyl formed were smaller, deuterium was incorporated into these products more extensively than was observed in the D_2-CO-H_2O system. Although not shown in the figure, the spectra of the unreacted dibenzothiophene obtained from the experiments carried out in the H_2-CO-D_2O and N_2-D_2O systems indicated that they were all D-substituted species containing d_1, d_2, d_3, and d_4 species. However, it was observed that the unreacted dibenzothiophene obtained in the D_2-CO-H_2O system was nothing but the d_1 species.

The extensive H/D exchange observed between dibenzothiophene and D_2O under N_2 pressure is consistent with the results reported by Kabe et al[6] dealing with hydrogen exchange of H_2O with coal or phenolic model compounds. In the case dealing with hydrogen exchange between syngas-H_2O and dibenzothiophene, the situation is not the same. Water participates in the water-gas shift reaction as evidenced by the formation of CO_2. It is expected that the D_2O in the syngas-D_2O system reacts with CO to form active deuterium which leads to the formation of D_2, and in the process, some active deuterium may be incorporated into dibenzothiophene and the substrates.

To observe the extent of D atoms from D_2O transfer back to form dihydrogen such as HD and D_2 in gaseous products, the gases were analyzed by gas chromatograph and quadrapole mass spectrometer. The analytical results are given in Table 4. It is noted that some deuterium in D_2O is present in HD and D_2 in the syngas-D_2O system, while no deuterium is present in the "hydrogen gases" of the gaseous products in the N_2-D_2O system. A small amount of H_2 formed in the N_2-D_2O system may have come from the dehydrogenation or decomposion of the solvent and reactant. In contrast to the experiment in the H_2-CO-D_2O system where HD and D_2 were formed , the experiment in the D_2-CO-H_2O system yielded gasous products containing HD and H_2 in the "hydrogen gases". These results indicate that, unlike D_2O in the N_2-D_2O system, D_2O in the syngas-D_2O system or H_2O in the D_2-CO-H_2O system forms active deuterium or hydrogen, respectively, which in turn is incorporated into the reactant and substrates or leads to the formation of HD and D_2 or HD and H_2, respectively. In the N_2-D_2O system, most deuterium is probably incorporated into the reactant by exchange reactions. It may then be concluded that both gas-phase hydrogen and hydrogen formed via the water-gas shift reaction in the syngas-H_2O system contribute to hydrodesulfurization, and the accompanying water-gas shift reaction is benefitial in reducing H_2 consumption.

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Table 1. Hydrodesulfurization of Dibenzothiophene
(Catalyst:$NiMo/Al_2O_3$, Initial Press:70 kg/cm², Temp:400 ℃, Time:45 min)

Gas system	H_2			H_2-CO-H_2O (1:1:0.3)		
Solvent	Decalin	Tetralin	Decalin + 1-methyl-naphthalene	Decalin	Tetralin	Decalin + 1-methyl-naphthalene
Dibenzothiophene conv., %	94.2	94.1	94.8	74.8	77.1	80.4
Bicyclohexyl formed, %	7.4	3.8	3.8	0.3	1.2	1.0
Cyclohexylbenzene formed, %	24.8	32.6	30.8	21.2	21.1	16.6
Biphenyl formed, %	33.6	39.5	43.8	42.0	44.0	54.5
Decalin remained, %	84.2	16.9[a]	83.8	91.2	4.3[a]	89.4
trans/cis ratio	4.8	4.0	4.5	4.0	3.7	4.1
Tetralin formed, %	2.9	67.2[b]	5.0	3.8	75.3[b]	4.8
Naphthalene formed, %	0.2	7.0	1.6	1.1	18.4	2.0
1-Methylnaphthalene remained, %	-	-	22.9	-	-	51.5
CO conv., %	-	-	-	32.5	40.3	39.8
H_2 consump., wt% of dibenzothiophene	5.2	6.0	7.3	2.0	2.0	3.4

[a] Decalin formed
[b] Tetralin remained

Table 2. Hydrodesulfurization Using Syngas at Various H_2/CO/H_2O Mole Ratios
(Catalyst:$NiMo/Al_2O_3$, Solvent : Decalin, Temp:400 ℃, Time:45 min)

Syngas-H_2O	H_2-CO-H_2O (1:1:0.3)	H_2-CO-H_2O (1:1:0.6)	H_2-CO-H_2O (1:1:1)	H_2-CO-H_2O (2:1:0.6)	H_2-CO-H_2O (3:1:0.6)
Initial syngas press., kg/cm²	70	63	55	70	70
Dibenzothiophene conv., %	74.8	72.0	63.7	78.7	81.0
Bicyclohexyl formed, %	0.3	1.5	0.6	2.5	2.8
Cyclohexylbenzene formed, %	21.2	20.6	14.6	24.1	26.1
Biphenyl formed, %	42.0	41.5	44.5	36.7	36.8
Decalin remained, %	91.2	92.2	92.2	91.4	92.8
trans/cis ratio	4.0	4.0	3.8	4.3	4.3
Tetralin formed, %	3.8	4.1	4.6	3.0	3.2
Naphthalene formed, %	1.1	1.1	1.9	0.4	0.5
CO conv., %	32.5	34.7	26.6	25.8	35.3
H_2 consump., wt% of dibenzothiophene	2.0	0.9	0.1	1.6	2.7
H_2/CO ratio after the reaction	1.5	1.6	1.4	2.7	5.2

Table 3. Hydrodesulfurization Using Syngas-D_2O or Deuterium Containing Gases
(Catalyst:$NiMo/Al_2O_3$, Solvent:Decalin, Temp:400 ℃, Time:45 min)

Gas system	H_2-CO-D_2O (1:1:1)	D_2-CO-H_2O (1:1:1)	N_2-D_2O (2:1)
Initial press., kg/cm²	40	40	40
Dibenzothiophene conv., %	74.5	69.5	35.0
Bicyclohexyl formed, %	0.6	0.3	trace
Cyclohexylbenzene formed, %	14.1	11.4	0.2
Biphenyl formed, %	43.9	45.4	27.2
Decalin remained, %	84.0	87.0	82.6
trans/cis ratio	3.8	4.0	2.2
Tetralin formed, %	5.5	5.3	3.7
Naphthalene formed, %	2.5	2.9	7.1
CO conv., %	30.1	23.3	-

Table 4. G.C. and M.S. Analysis of Gaseous Products

Gas system	H_2-CO-D_2O	D_2-CO-H_2O	N_2-D_2O
Gaseous Products*, mol %			
CO	40.1	35.2	-
CO_2	15.0	12.7	-
N_2	-	-	94.9
Hydrogen	41.3	48.7	3.6
(H_2)	(63)	(13)	(100)
(HD)	(31)	(11)	0
(D_2)	(6)	(76)	0

* The remainders are CH_4, C_2H_6, and H_2S.

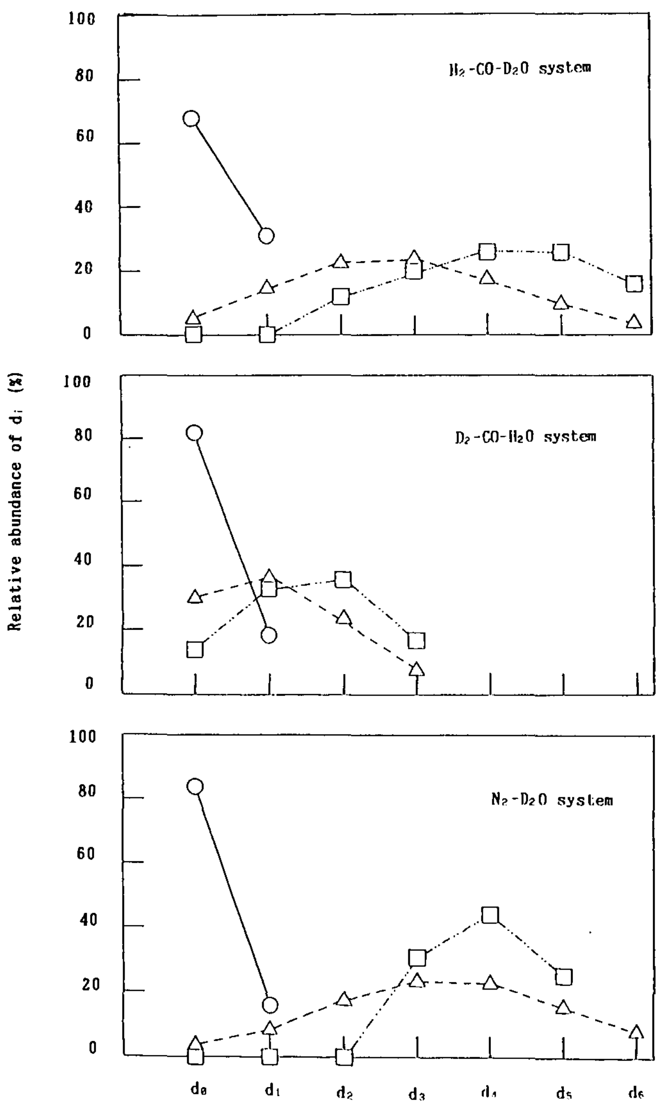

Figure 1 Distribution of deuterium in solvent and products
○ t-Decalin △ Biphenyl □ Cyclohexylbenzene